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(54) **Process for the isomerization of butenes**

(57) A process for the isomerization of n-butenes into isobutenes comprising contacting an n-butene containing feedstock with a catalyst consisting of crystalline silica polymorph of the silicalite type, in the presence of steam, with a molar ratio water: feed of from 0.5 to 5.

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SPECIFICATION

Process for the isomerization of olefins

5 The present invention relates to a process for the isomerization of olefins. More particularly, it concerns a process for the isomerization of n-butenes into isobutene.

Measures which have been adopted to ban
10 the use of lead tetraethyl in fuels have lead the petroleum industry to study other additives, particularly oxygenated additives, which improve the octane number of fuels. Some of these additives have been found to be very
15 effective, particularly the asymmetric ethers and specifically methyl tert-butyl ether (or MTBE). MTBE is prepared from methanol and isobutene.

Isobutene is also used as raw material for
20 the production of other valuable compounds, such as tert butyl alcohol (solvent), tert-butyl-phenol (stabilizer), low molecular weight polymers (viscosity improvers of lubricating oil). However, the present capacity for producing
25 isobutene does not provide sufficient amount of these derivatives to satisfy the potential market.

There is therefore a need for a process which enables isobutene to be produced simply and economically.

An object of the present invention is to provide a new process for the production of isobutene.

According to the present invention there is
35 provided a process for the isomerization of n-butenes into isobutene which process comprises contacting an n-butene containing feed with a catalyst consisting of a crystalline silica polymorph of the silicalite type, in the presence of steam, the molar ratio of water: feed
40 being from 0.5 to 5.

The starting feedstock for the process of the invention may be substantially pure 1-butene or 2-butene; or mixtures of both these isomers, or even fractions which contain these
45 isomers in admixture with other hydrocarbons. The process of the invention may be applied to feeds having an n-butene content as low as 10% by volume.

50 The catalyst is an unmodified crystalline silica polymorph of the silicalite type. It is therefore a substantially pure silica, that means that said silica does not contain any impurity or any modifier, except traces
55 thereof. A method for preparing silicalite, and the structure of silicalite, are disclosed in U.S. Patent 4,061,724 (Grove), incorporated herein by reference.

The n-butene-containing feedstock is contacted with silicalite in the presence of steam.
60 It is known that silicalite is used as catalyst for the oligomerization of olefins, as disclosed in U.S. Patents 4,414,423; 4,417,086 and 4,417,088 of S. J. Miller incorporated herein
65 by reference. However, it has unexpectedly

been found that the presence of water not only increases the life of the catalyst, but particularly favours the production of isobutene while reducing the formation of heavier products. Owing to the presence of steam, the isobutene selectivity is increased by about 50%, all other factors being equal. The term "isobutene selectivity" means the weight of formed isobutene calculated on 100 parts by
70 weight of converted feed. At the lower end of the range, an improvement in selectivity is obtained when the treatment of the feed is carried out in the presence of an amount of water of about 0.5 mole of water per mole of feed. Comparative experiments have also
75 shown that it is preferable to maintain a molar ratio of water: feed which does not exceed about 5. This higher limit varies with the composition of the feed. The molar ratio of water: feed is preferably lower than about 1.5 when the treated feed has a n-butene content of about 10% by volume. Generally the amount of water to be used is such that the molar ratio water: feed is from 0.5 to 3;
80 said ratio may however be higher if the feed has a high n-butene content.

The process of the invention is very flexible and it may be carried out in the gaseous phase and/or in the liquid phase.

95 The reaction temperature is generally from 300 to 550°C. Temperatures lower than 300°C give only very low yields, while temperatures higher than 500°C lead to a degradation of the reaction products.

100 Generally, the temperature is from 300 to 500°C, and more particularly from 320 to 475°C.

A variation of temperature between these limits does not give any substantial variation of the distribution of the formed products.

105 The hourly space velocity of the reaction mixture, expressed by the weight of said mixture treated by weight of catalyst in one hour (WHSV), may vary from 5 to 150. It typically depends on the composition of the feed. A high hourly space velocity improves the selectivity of the process for the formation of isobutene. When a feedstock which essentially consists of n-butene is used, a WHSV of from
110 5 to 100 is used, while with a feedstock which contains about 10% of n-butene, a WHSV of from 5 to 20 is used.

The reaction is generally carried out at an absolute pressure which may vary between wide limits, generally ranging from subatmospheric pressures to 50 bars.

Typical gauge pressures are from 0.5 to 20 bars.

120 It is advantageous to operate at not very elevated pressures to favour the production of isobutene.

A man skilled in the art will readily be able to determine the operating conditions, within the above-mentioned ranges, which lead to the best yields as a function not only of the
130

composition of the treated feedstock, but also of the desired results. Certain conditions, particularly a high WHSV, favour the formation of isobutene with a low conversion rate of the feed. In these conditions, it is advantageous to recover the isobutene from the reaction products and to recycle these later to submit them to an additional treatment in the presence of fresh feed.

10 The process of the present invention may be combined with the process disclosed in our co-pending Patent Application (Our Ref: 56592) filed on even date herewith and entitled "Process for producing isobutene". In 15 this latter process, a propylene-containing feed is converted into a mixture containing isobutene and n-butenes, besides other hydrocarbons. After optionally recovering isobutene, the mixture may be treated with the process 20 of the invention in order to improve the production rate of isobutene.

The following Examples are given to illustrate, but not limit, the process of the present invention.

25 Example 1

1-butene was passed together with steam over silicalite at a temperature of 302°C and under an absolute pressure of 1 bar, with a 30 molar ratio water:feed of 3.42 and a WHSV of 6.22.

85.6% of 1-butene was converted and the selectivity in isobutene was 13.33%.

By way of comparison, a similar experiment 35 was carried out but in the absence of water. The selectivity in isobutene was only 7.79%.

Example 2

The procedure of Example 1 was repeated, 40 but with a molar ratio water:feed of 1.66.

85.8% of 1-butene was converted and the selectivity in isobutene was 12.95%.

Example 3

45 A feed containing 60% by weight of isobutane and 40% by weight of n-butenes, was passed together with steam over silicalite at a temperature of 319°C, at a gauge pressure of 2 bar, a WHSV of 5.3 and a molar ratio 50 water:feed of 0.88. 86.6% of butenes was converted and the selectivity in isobutene was 15.61%.

Example 4

55 A feed containing 49% by weight of n-butenes, 49.6% by weight of n-butane and 1.4% by weight of light hydrocarbons, was passed together with steam over silicalite at a temperature of 425°C, an absolute pressure 60 of 1.6 bar, a WHSV of 31.1 and a molar ratio water:feed of 1.16.

78.2% of butenes was converted and the selectivity in isobutene was 14.03%.

65 Example 5

A feed containing 49% by weight of n-butenes, 49.6% by weight of n-butane and 1.4% by weight of light hydrocarbons was passed together with steam, over silicalite at a 70 temperature of 325°C, an absolute pressure of 1.6 bar, a WHSV of 31.4 and a molar ratio water:feed of 1.11.

79.4% of butenes was converted and the selectivity in isobutene was 12.5%.

75 This example shows that in the considered range of temperatures from 300 to 500°C, a temperature variation has practically no influence on the distribution of the formed products.

80 By way of comparison, the same feed was treated but in the absence of steam, while maintaining the other operating conditions:

-temperature	:	322°C
85 -absolute pressure	:	14.8 bar
-WHSV	:	33.2

89% of butenes was converted but the selectivity in isobutene was only 5.99%.

90 This example shows that the selectivity in isobutene is very low when the reaction is carried out in the absence of water.

CLAIMS

95 1. Process for the isomerization of n-butenes into isobutene which process comprises containing an n-butene containing feed with a catalyst consisting of a crystalline silica polymorph of the silicalite type, in the presence of 100 steam, the molar ratio of water:feed being from 0.5 to 5.

2. Process according to Claim 1, wherein the molar ratio of water:feed is from 0.5 to 3.

3. Process according to Claim 1 or 2, 105 wherein the reaction temperature is from 300°C to 550°C.

4. Process according to Claim 3, wherein the reaction temperature is from 300°C to 500°C.

110 5. Process according to Claim 4, wherein the reaction temperature is from 320°C to 475°C.

6. Process according to any one of the preceding Claims, wherein the amount of reaction mixture treated expressed by weight 115 per hour per weight of catalyst (WHSV) is from 5 to 150.

7. Process according to Claim 6, wherein the WHSV is from 5 to 100.

120 8. Process according to any one of the preceding Claims, wherein the reaction is carried out at an absolute pressure ranging from a subatmospheric pressure to 50 bars.

9. Process according to Claim 8, wherein 125 the reaction is carried out at an absolute pressure of from 0.5 to 20 bars.

10. Process according to Claim 1 substantially as hereinbefore described in any one of Examples 1 to 5.

130 11. Isobutenes whenever obtained by a

process as claimed in any one of the preceding Claims.

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